

Geochemical applications in petroleum systems analysis: new constraints and the power of integration

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Abstract: This paper provides an overview of the role that geochemistry plays in petroleum systems analysis, and how this can be used to derive constraints on the key elements and processes that give rise to a successful petroleum system. We discuss the history of petroleum geochemistry before reflecting on the next frontier in geochemical applications in hydrocarbon systems. We then review the individual contributions to this Special Publication. These papers present new geochemical techniques that allow us to develop a more systematic understanding of critical petroleum system elements; including the temperature and timing of source-rock deposition and maturation, the mechanisms and timescales associated with hydrocarbon migration, trapping, storage and alteration, and the impact of fluid flow on reservoir properties. Finally, we provide a practical example of how these different geochemical techniques can be integrated to constrain and generate a robust understanding of the prolific Paleozoic petroleum system of the Bighorn Basin.



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By 2035, global energy demand is anticipated to increase by 33% as the population continues to grow (WEO 2011; Khatib 2012). While renewable energy sources are expanding rapidly, hydrocarbons are predicted to supply 80% of the global demand until at least 2040 (Khatib 2012; ExxonMobil 2016). Historically, increases in energy demand have driven oil and gas companies to transition hydrocarbon exploration towards increasingly complex environments. Beginning in the 1900s and through to the 1950s, oil and gas exploration was largely focused towards onshore assets. A move to shallow offshore environments in the 1960s preceded a shift to ultra-deep-water (>1500 m) environments in the 1980s in regions such as West Africa and the Gulf of Mexico (May *et al.* 2010). To meet future energy demand, exploration is again moving into increasingly challenging geological settings, such as tight/unconventional resources, deep targets in ultra-deep-water basins, salt basins where subsurface imaging is extremely difficult, and harsh and environmentally sensitive drilling environments such as the Arctic (Summa 2015). Exploration companies must also contend with technical and drilling challenges associated with shallow gas in deep-water settings, heavy oil and potentially corrosive non-hydrocarbon gases, such as CO₂ and H₂S.

While exploration environments and technical challenges have evolved, the key questions asked of the petroleum systems analyst have remained broadly the same since Colonel Edwin Drake struck oil at a depth of 69 ft in Titusville, Pennsylvania, USA in 1859 (Link 1952). This is true both in frontier basins with no prior history of exploration, and in mature basins with thousands of wells. The first and most important question asked of the exploration geologist is whether a petroleum system (thermogenic or biogenic) exists. In other words, is there an organic-rich rock buried to sufficient temperature and pressure to generate hydrocarbons? Or is there a robust biogenic gas system?

If evidence suggests hydrocarbons were generated, the petroleum systems analyst must determine whether they were trapped and, if so, is the accumulation dominantly oil or gas. In systems where a robust petroleum system has been demonstrated and subsurface accumulations have been discovered, a more challenging question arises when a drilled well yields negative results: why was this well dry? This becomes even more challenging when one considers the potential for purely biogenic gas occurrences that are not associated with a thermogenic hydrocarbon system.

Biogenic gas accumulations represent some of the largest recent gas discoveries (e.g. the Zohr

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Field, Egypt: [Esestime et al. 2016](#)) and globally may represent up to 20–30% of all natural gas resources ([Grunau 1984](#); [Whiticar et al. 1986](#); [Rice 1993](#)). [Odedra et al. \(2005\)](#) estimated that if only 10% of the microbially produced methane is trapped, it would provide a resource base of 20 000 trillion cubic ft (TCF). These estimates are conservative as they are dominated by primary microbial gas and do not include potentially vast volumes of secondary microbial gas as proposed in the West Siberian Basin ([Milkov 2010](#)). Overall, these estimates are poorly constrained due to the difficult nature of predicting the generation and accumulation of microbial gas over geological timescales. However, even with the inherent complexities in understanding biogenic gas systems, the volumes of microbial gas can be of great economic value and the key question that remains is: What are the principal elements that give rise to large biogenic gas accumulations, and how can we develop an effective exploration strategy to discover them? Regardless of thermogenic or biogenic origin, the petroleum systems analyst needs a framework and set of tools to evaluate exploration opportunities and risk of the presence of a working hydrocarbon system.

It has been over 20 years since [Magoon & Dow \(1994\)](#) laid the foundation for petroleum systems analysis as an integrated science. They defined the petroleum system as:

[A] natural system that encompasses a pod of active source rock and all related oil and gas and which includes all the geologic elements and processes that are essential if a hydrocarbon accumulation is to exist. The term *system* describes the interdependent elements and processes that form the functional unit that creates hydrocarbon accumulations. The *essential elements* include a petroleum source rock, reservoir rock, seal rock, and overburden rock, and the *processes* are trap formation and the generation-migration-accumulation of petroleum. These essential elements and processes must occur in time and space so that organic matter included in a source rock can be converted to a petroleum accumulation. A petroleum system exists wherever the essential elements and processes occur.

Geochemical techniques have contributed significantly to our understanding of petroleum systems globally. However, to meet the increasing challenges of discovering new hydrocarbon resources, it is essential we continue to advance our understanding of these systems through new geochemical approaches and analytical developments. Such development requires that academic and industry-led research efforts converge in ways that are unique to the geosciences. This Special Publication arose from the session of the same name at Goldschmidt 2015, and presents contributions that incorporate non-traditional geochemical and isotopic techniques, specifically recent advancements in carbonate and

hydrocarbon clumped and position-specific isotope geochemistry, noble gas geochemistry, trace element geochemistry, isotope chemistry of heavy elements, and molecular geochemistry.

The aim of this volume is not to simply present new techniques, but to showcase how recent advances and state-of-the-art approaches in geochemistry from both industry and academia can generate new ways of thinking about old problems. Techniques and approaches presented herein focus on addressing three key hydrocarbon systems issues: (1) source-rock identification and the temperature/timing of hydrocarbon generation ([Eiler et al. 2017](#); [Gao et al. 2017](#); [Pedentchouk & Turich 2017](#); [Stolper et al. 2017](#)); (2) the mechanisms and timescales associated with hydrocarbon migration, trapping, storage and alteration ([Byrne et al. 2017](#); [Moore et al. 2018](#)); and (3) the impact of fluid flow on reservoir properties ([MacDonald et al. 2017](#)).

While this volume focuses on how new geochemical techniques can be used in petroleum systems analysis, we also recognize the potential uplift that these same techniques could offer in the environmental sciences. Increased environmental awareness means that new and increasingly sophisticated approaches are required to ensure that human activities, such as resource exploration and extraction, have a minimal impact on the natural environment. Two of the most obvious challenges in this respect is the reduction of greenhouse gas emissions that contribute to global climate change and the protection of potable water resources. Almost all studies addressing environmental questions contain an element of forensic fingerprinting and reconstruction, and the geochemical tools discussed in this Special Publication are likely to play an important role in this evolving landscape. For example, the carbonate clumped isotope technique applied in [MacDonald et al. \(2017\)](#) could also be used to study the cementation history of aquifers targeted for managed aquifer recharge (MAR), a strategy of using aquifers to store and improve the quality of water for future use ([Maliva et al. 2015](#)). The noble gases discussed in [Byrne et al. \(2017\)](#), and applied in [Moore et al. \(2018\)](#), are already a well-established technique studying geological sequestration of carbon dioxide and other gases (e.g. [Gilfillan et al. 2009](#)). Finally, the isotopic approaches described in [Eiler et al. \(2017\)](#), [Gao et al. \(2017\)](#), [Pedentchouk & Turich \(2017\)](#) and [Stolper et al. \(2017\)](#) all have the capability to elucidate the origin of hydrocarbons in the environment.

In this introductory chapter, we first provide a brief history of petroleum geochemistry and its application in petroleum system analysis. We then introduce a new generation of geochemical techniques that are discussed in different chapters of this Special Publication. Finally, we provide a case

study from the Bighorn Basin that integrates traditional and new geochemical exploration techniques to generate new petroleum systems concepts for the prolific Paleozoic petroleum system.

The first wave of geochemical tools for petroleum systems analysis

Petroleum geochemistry has played an important role in hydrocarbon exploration for over 50 years (Hedberg 1964). However, even before petroleum geochemistry became established as a field, and before characterization of oils and gases was possible, scientists pondered the origin of hydrocarbons. Perhaps, the first person to propose the now accepted concept that economic accumulations of hydrocarbons have an organic origin was Thomas S. Hunt. He suggested that organic matter in North American Paleozoic rocks, which he believed was the precursor of local hydrocarbon accumulations, was likely to be derived from marine vegetation or the remains of marine animals (Hunt 1861). Decades later, Wallace Pratt, the former Chief Geologist of Humble Oil (which ultimately became ExxonMobil) was an early adopter of petroleum geochemistry principles. He popularized the concept that small hydrocarbon molecules were formed from larger parent molecules as a result of thermal cracking at depth (Pratt 1943). This is one of the guiding principles from which predictions of commodity type (oil v. gas) are now based. However, it was not until almost 100 years after Hunt introduced the organic origin of hydrocarbons hypothesis that it became widely accepted, when geochemical (Treibs 1936; Eglinton & Calvin 1967) and isotopic evidence (Craig 1953) provided compelling evidence in support of the theory. These early days of proto-petroleum geochemistry laid the foundations that future developments in analytical capabilities would allow us to investigate.

Prior to the 1980s, analytical and technological limitations restricted our ability to appreciate the many ways in which geochemistry could contribute to petroleum systems analysis. This changed in the 1980s and 1990s, when a series of geochemical tools were developed that provided important information about petroleum systems. To list and describe each of these contributions is beyond the scope of this review. We highlight here a small selection of the developments that we consider to have contributed significantly to petroleum systems analysis. A more detailed history of petroleum geochemistry can be found in Hunt *et al.* (2002) and Kvenvolden (2006, 2008). Similarly, we refer the interested reader to Tissot & Welte (1984) and Hunt (1996), seminal publications that describe the breadth and scope of petroleum geochemistry.

Advances in analytical organic geochemistry, specifically high-resolution gas chromatography and mass spectrometry, and newly recognized biological markers provided the first step-change in our ability to constrain the origin and post-formational history of liquid hydrocarbons through empirical observations of source rocks and oils. Through these advances, it became possible to: (i) determine the organic matter type and depositional environment of a source rock (e.g. Mackenzie *et al.* 1984; Tissot & Welte 1984; Moldowan *et al.* 1985; Peters *et al.* 1986, 2005); (ii) quantify the thermal maturity of a source rock (e.g. Tissot *et al.* 1987; Waples 1994); (iii) constrain the age of the source rock from which oil has been generated (e.g. Moldowan *et al.* 1994; Holba *et al.* 1998); (iv) identify and qualitatively estimate the extent of post-generation alteration, such as biodegradation (e.g. Wenger *et al.* 2002) and thermochemical sulphate reduction (Zhang *et al.* 2007); and (v) genetically link reservoir or seeped oils with other oils or to the source rocks from which they were generated (e.g. Curiale 1994). These developments also prompted comprehensive experimental studies to understand the processes, timescales and temperatures associated with source-rock maturation, hydrocarbon generation and expulsion from source rocks (e.g. Lewan 1985, 1994; Vandenbroucke *et al.* 1999). A central concept to many of these studies is that the generation of hydrocarbons is a unidirectional, kinetically controlled process. These advances in our ability to model hydrocarbon generation and characterize fluids and rocks to constrain their origin and depositional history have significantly improved our understanding of the petroleum system. One of the broader implications of this is that we are now able to calibrate geological models away from the well in which the sample was obtained to predict the potential distribution of oil v. gas within a basin, constrain the relative timing of maturation to other key petroleum systems elements such as reservoir deposition and structure timing, and, ultimately, to develop predictions of the location and hydrocarbon properties of potential accumulations.

At the same time, the use of chemical and isotopic signatures of natural gases also became well established in hydrocarbon exploration. Of particular importance in these early years of gas geochemistry applications in the petroleum industry were two specific capabilities: (i) being able to distinguish thermogenic gases from those that are generated by microbial processes (e.g. Bernard *et al.* 1976; Schoell 1980; Rice & Claypool 1981); and (ii) the ability to estimate the thermal maturity of a source rock from the carbon ($\delta^{13}\text{C}$) and hydrogen (δD) isotopic signature of hydrocarbon gases (e.g. Whiticar 1994).

The 1980s and 1990s also saw significant advances in our ability to constrain the thermal

history of sedimentary basins. This included the development of: (i) fluid-inclusion microthermometry (e.g. Goldstein & Reynolds 1994), which provides key constraints on the maximum burial temperature, and can be used to constrain the timing of hydrocarbon charge; (ii) vitrinite reflectance (e.g. Barker & Pawlewicz 1986), which can help constrain both the maximum temperature and time-integrated maturity of any given stratigraphic interval; and (iii) thermochronology techniques, such as illite age analysis (e.g. Pevear 1992, 1998) and U–Th/He dating (e.g. Farley *et al.* 1996; Wolf *et al.* 1996, 1997) that can be used to constrain both the burial and uplift phases of a basin history, respectively. This information provides previously unavailable calibration parameters that can now be utilized by advanced computing tools to calibrate more realistic models of basin thermal evolution. The most advanced tool in this regard is four-dimensional (4D) basin modelling, which models the evolution of a sedimentary basin in 3D space through time. These models are often the major platform for integrating information provided by not only geochemistry, but also geophysical techniques. When integrated with an understanding of the regional geology, such models can be used to make improved predictions of the spatial and temporal properties of key hydrocarbon systems elements and processes. These elements include regional source-rock maturation, hydrocarbon generation timing, hydrocarbon migration pathways and the preservation or deterioration of reservoir quality. A detailed discussion of such models is beyond the scope of this chapter, and as such we refer the interested reader to Hantschel & Kauerauf (2009) and Nemčok (2016).

The new frontier in geochemical applications in petroleum systems analysis

One of the significant challenges for the next decade is the requirement to work with increasingly small and limited datasets in frontier environments. As such, there is a need to generate a greater depth of information from what few samples are available. As is often the case, such advances require a significant improvement in analytical capabilities and more sophisticated approaches to obtaining and understanding data. Developments over the past decade in high-resolution Fourier transform (e.g. FT-ICR-MS: Oldenburg *et al.* 2015) and multicollector mass spectrometry (e.g. high-resolution isotope ratio mass spectrometry: Eiler *et al.* 2013), and new approaches to mining increasingly large datasets have risen to meet this challenge. These techniques now allow the geochemist to probe samples with greater precision and specificity down to

the atomic level, and have triggered a renaissance of innovation in petroleum geochemistry. The following section introduces some of the techniques that have developed during this period and how these can be applied in petroleum systems analysis.

Clumped isotope thermometry of carbonates represents a step-change from the traditional thermometry techniques described above, such as fluid-inclusion microthermometry, vitrinite reflectance and thermochronology. The development of high-resolution isotope ratio mass spectrometers has, for the first time, provided an opportunity to investigate the temperature dependence of multiple isotopic substitutions in both inorganic and organic molecules (Ghosh *et al.* 2006; Eiler 2007; Eiler *et al.* 2013; Stolper *et al.* 2014a, b). The carbonate clumped isotope thermometer was the first of the new suite of thermometers, and has been demonstrated to be applicable in the 50–300°C range, which is therefore relevant to processes such as dolomitization (Ferry *et al.* 2011) and burial diagenesis (Huntington *et al.* 2011; Shenton *et al.* 2015; Lawson *et al.* 2017). Information from this thermometer helps constrain the thermal history of sedimentary basins, and predictions of the preservation or destruction of porosity and permeability in carbonate reservoirs. In this volume, MacDonald *et al.* (2017) present a detailed clumped isotope study from a carbonate reservoir offshore Angola to show that carbonate clumped isotope geochemistry can yield new insights on the temperature and timing of dolomitization.

In addition to the carbonate thermometer, further developments in high-resolution multicollector mass spectrometry (e.g. Eiler *et al.* 2013) have resulted in the development of the first hydrocarbon clumped isotope geothermometer (Stolper *et al.* 2014a). The $^{13}\text{CH}_3\text{D}$ isotopologue of methane records and preserves the generation temperature of methane in both biogenic and thermogenic systems (Ono *et al.* 2014; Stolper *et al.* 2014a, b, 2015; Wang *et al.* 2015). Also in this volume, Stolper *et al.* (2017) review the current state-of-the-art in methane thermometry and describe potential new applications in hydrocarbon exploration. While the methane body of work represents the most significant to date in hydrocarbon clumped isotope and position-specific geochemistry, significant steps forward are being made in our understanding of the history of larger hydrocarbons. For example, it is now possible to measure ^{13}C – ^{13}C clumping in ethane, and a preliminary dataset has now been reported in Clog *et al.* (2018). Similarly, three independent techniques have been developed to measure the ^{13}C position-specific signatures of propane (Gao *et al.* 2016; Gilbert *et al.* 2016; Piasecki *et al.* 2016). Eiler *et al.* (2017), in this volume, review published and unpublished work on the isotopic anatomy of organic molecules larger than methane, and outline potential

future constraints offered by clumped isotope and site-specific analysis of organic molecules (e.g. biosynthesis, maturation, and the environmental conditions of hydrocarbon generation and storage).

Noble gas geochemistry, unlike clumped isotope geochemistry described above, has a longer history in petroleum systems analysis. However, the exploitation of unconventional resources over the past decade has provided a new natural laboratory to test some of the key hypotheses that are also relevant to conventional systems. While the other techniques discussed in this Special Publication are sensitive tracers of hydrocarbon origin, accumulation and alteration, the noble gases are chemically inert and as such do not partake in any chemical or biological reactions that may perturb the geochemical record of other tracers. Instead, they provide information on the physical interaction and mixing of fluids in the subsurface, and can yield constraints on the timescales associated with hydrocarbon storage. Prior applications of noble gas geochemistry focused on the role of groundwater flow in hydrocarbon migration (Zartman *et al.* 1961; Bosch & Mazor 1988; Ballentine *et al.* 1991; Barry *et al.* 2016) and cementation (Ballentine *et al.* 1996). Recent advances in multicollector mass spectrometry now provide increasingly sensitive measurements of noble gases with greater precision. This capability has many potential uses in petroleum systems analysis, and has recently been applied to develop accurate estimates of the residence time of fluids in Precambrian crust (Holland *et al.* 2013) and in hydrocarbon accumulations of northern Germany (Barry *et al.* 2017). In this volume, Byrne *et al.* (2017) take a new look at how noble gas geochemistry can be used to constrain the migration and accumulation history of hydrocarbons, with a particular focus on unconventional accumulations that have only recently begun to be studied (e.g. Hunt *et al.* 2012) despite the fact that these resources have been intensely developed over the last 10 years. Also in this volume, Moore *et al.* (2018) describe how noble gases can be used to determine the history of hydrocarbons and the origin of non-hydrocarbon gases, such as H₂S, in unconventional resources, with a case study from the Illinois Basin.

Molecular geochemistry is, perhaps, the most widely applied technique in petroleum systems analysis. Among other applications, it is routinely used to tie oils to specific source intervals during exploration, to determine if oils are connected laterally within reservoir intervals to guide development of discovered hydrocarbons, and to determine the composition of oils, which governs the ultimate value of any accumulation that is going to be produced. However, like all other techniques, this approach also has its limitations. For example, molecular geochemistry may be unable to tie oil to a specific source interval if

there are multiple source rocks in the basin with similar molecular signatures. Such a scenario is made more difficult by the fact that a relative paucity of biomarkers have been discovered that provide definitive and high-resolution age constraints on source rock age. This is a common challenge for the petroleum systems expert in frontier basins with multiple Jurassic or Cretaceous marine clastic source intervals that could all plausibly be the source of hydrocarbons encountered during the initial stages of exploration. Recent advances in established techniques, such as compound specific isotope analysis, may finally provide a path to constraining such systems. Pedentchouk & Turich (2017), in this volume, review the history of compound-specific carbon and hydrogen isotope analysis of hydrocarbons, and how such data can be used in exploration activities. They provide several case-study examples of how this technique has been used to better understand the origin of hydrocarbons in systems where conventional molecular geochemistry alone may not provide unambiguous results.

Finally, recent developments in the analysis of the isotopic signatures of heavy metals, such as rhenium, osmium, vanadium, nickel and molybdenum (e.g. Ventura *et al.* 2015; Georgiev *et al.* 2016), now provide new constraints on the origin and history of hydrocarbons. The study by Gao *et al.* (2017) in this volume reports on some of the first results of vanadium isotope (⁵¹V/⁵⁰V) analysis of oils. This study discusses the main controls on the isotopic system, and how this can be applied to provide new constraints on the origin and history of oils in petroleum systems studies.

Bighorn Basin petroleum systems study: the power of integration

In the preceding sections, we have described the history of geochemistry in petroleum systems analysis, and what insights can be gained from individual techniques. However, it is only when this information is integrated can one really develop a holistic understanding of all elements and processes that contribute to a successful petroleum system. We will dedicate the following section to providing a case example of how this may be achieved for a prolific hydrocarbon system. As a laboratory for this approach, we use the Bighorn Basin of north-central Wyoming (Fig. 1), one of several significant petroleum-bearing basins in the Rocky Mountain Province of the western USA. The Bighorn Basin has produced over 2 billion barrels of oil and minor gas since the early 1900s (De Bruin 1997). After more than 100 years production is on the decline and there is limited exploration activity. Nonetheless, the wealth of existing data makes this

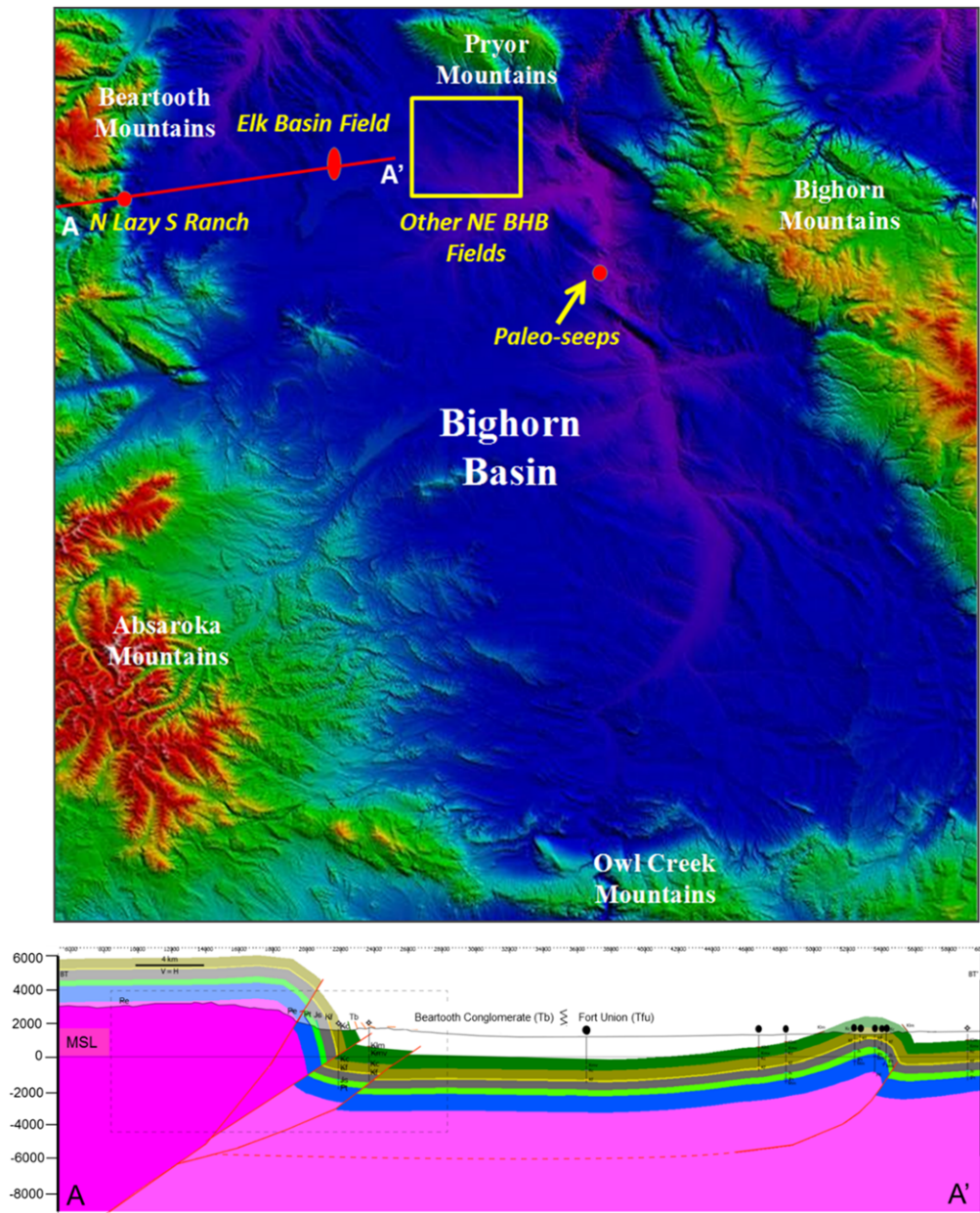


Fig. 1. Digital elevation map and representative structural cross-section for the Bighorn Basin showing sample localities describe in the text. The basin is bounded on all sides by Precambrian basement uplifts of 10 000–12 000 ft elevation (Beartooth Mountains, Pryor Mountains, Bighorn Mountains and Owl Creek Mountains), and by Tertiary volcanic rocks of the Absaroka Mountains. The basin is filled with up to 25 000 ft of sediments of Paleozoic (blue), Mesozoic (green, brown) and Tertiary (yellow) ages. Large basement-involved reverse faults define the basin edges and form anticlinal structures that serve as traps for hydrocarbon accumulation. MSL, mean sea level.

basin an ideal laboratory in which to test the power of geochemical integration to new petroleum systems concepts.

This example begins with a fundamental genetic analysis of the basin (Fig. 2) and focuses on two major tectonic events associated with long-lived

plate convergence: (1) the Cretaceous Sevier Orogeny, in which convergence drove thin-skinned thrusting and development of a broad foreland basin; and (2) the Early Tertiary Laramide Orogeny, in which increased convergence rates and shallowing subduction drove thick-skinned deformation and the formation of basement-involved uplifts and intermontane basins (e.g. Sheldon 1967; Stone 1967). These events resulted in two petroleum systems in the Bighorn Basin: (1) a relatively 'simple' Mesozoic system in which local Mesozoic source rocks generate hydrocarbons that fill Mesozoic reservoirs during Early Tertiary trap formation; and (2) a more 'complex' Paleozoic system, in which hydrocarbons are likely to have migrated from the Sevier foredeep, at least partly prior to trap formation. Ironically, the relatively simple Mesozoic system has produced only approximately 10% of the basin's hydrocarbons, while the complex Paleozoic system has produced 90% (Stone 1967). We have integrated both traditional and novel geochemical approaches to better understand the success of the Paleozoic system.

We provide supporting evidence from key Paleozoic hydrocarbon systems elements of source distribution, maturation timing, and lateral migration timing and pathways in Figures 3–5. Palaeogeographical maps for key time intervals are coupled to source rock geochemistry and burial history analyses. Oils in Paleozoic reservoirs came from a clastic-starved carbonate source rock that correlates with organic-rich rocks in the Permian Phosphoria Formation (Fig. 3), a well-documented source rock in western North America with total organic carbon (TOC) values of >20% in northern Utah and eastern Idaho (e.g. Claypool *et al.* 1978). In the Bighorn Basin, the Phosphoria Formation was deposited on the shelf, and consists of a stack of shallow-marine limestones and redbeds with no source potential. This geographical position and associated lithofacies suggest that long-distance lateral migration was required to fill Bighorn Basin traps with oils sourced from the Phosphoria (Sheldon 1967; Stone 1967). The closest organic-rich Phosphoria Formation with no evidence of clastic input is c. 100 km west and SW of the Bighorn Basin, in the foreland of the Sevier orogenic system (Fig. 3).

The hinterland load of the Sevier system is likely to have driven these source rocks into the oil window, at which point oils began to migrate eastwards through the foreland (Cheney & Sheldon 1959; Campbell 1962; Sheldon 1967). We hypothesize that hydrocarbon migration began in the distal hinterland given its proximity to the sedimentary load from the Sevier Orogeny and progressed eastwards as the foreland advanced, from c. 180 to 80 Ma, based on multiple burial histories constructed for eastern Idaho and western Wyoming (e.g. Burtner

& Nigrini 1994; Maughan 1984; Stone 1967). This requirement for long-distance lateral migration is consistent with previous predictions from molecular geochemistry (e.g. Claypool *et al.* 1978). A 1D basin model was built for the footwall of the Meade Thrust, using ExxonMobil proprietary basin-modelling software, in order to capture the burial history of the Phosphoria Formation in the area where it is believed to be an effective source rock (T. Becker pers. comm. 2015) (Fig. 4). Model results suggest that the Phosphoria source rock probably reached the oil window at approximately 170 Ma at this location (Fig. 4). Becker (pers. comm. 2015) applied illite age analysis on diagenetic illite sampled from the Meade Thrust to confirm this hypothesis. Diagenetic illite forms at temperatures of approximately 90–100°C, which roughly corresponds to the temperatures required for the onset of oil and gas generation (Eslinger & Pevear 1988). K–Ar age dating of this illite yielded an age of 178.6 ± 8 Ma at this location (T. Becker pers. comm.). At this time there were several high-permeability units that could have served as lateral migration pathways for hydrocarbons from the Phosphoria Formation, and the foreland was sufficiently unstructured and simple at that time to allow long-distance migration to occur (see the crustal-scale cross-section in Fig. 4).

As noted above, the present-day Bighorn Basin and its associated anticlinal traps developed during the Early Tertiary, when the foreland was broken up in response to increased plate convergence rates. The timing of trap development is debated, but is thought to be coincident with the Laramide Orogeny at c. 85–55 Ma (e.g. Lillis & Selby 2013), and suggests that a significant fraction of long-distance hydrocarbon migration from the west occurred prior to trap formation. The Sevier Foreland System is thought to have been broken and disconnected by the Laramide-related basement-involved uplifts by approximately 55 Ma (e.g. Sheldon 1967; Stone 1967), as can be seen in the centre of the crustal cross-section (see Fig. 5). A 1D basin model built at the location of the Johnson Watson well in the Elk Basin (T. Becker pers. comm. 2015) (Fig. 5) captures the magnitude of this event. Apatite fission-track analysis of drill cuttings from the well confirms that at least 1 km of uplift occurred in the area beginning at c. 55 Ma. We note here that not all basin reconstructions predict uplift at this time in the basin history (e.g. Roberts *et al.* 2008), and so the development and distribution of these barriers to hydrocarbon migration may not be a basin-wide phenomenon. However, our model is consistent with the timing and approximate magnitude of uplift of another 1D model developed for this part of the basin presented in Hagen & Surdam (1984). Such a scenario typically presents a big risk for a successful petroleum system, even though this system works

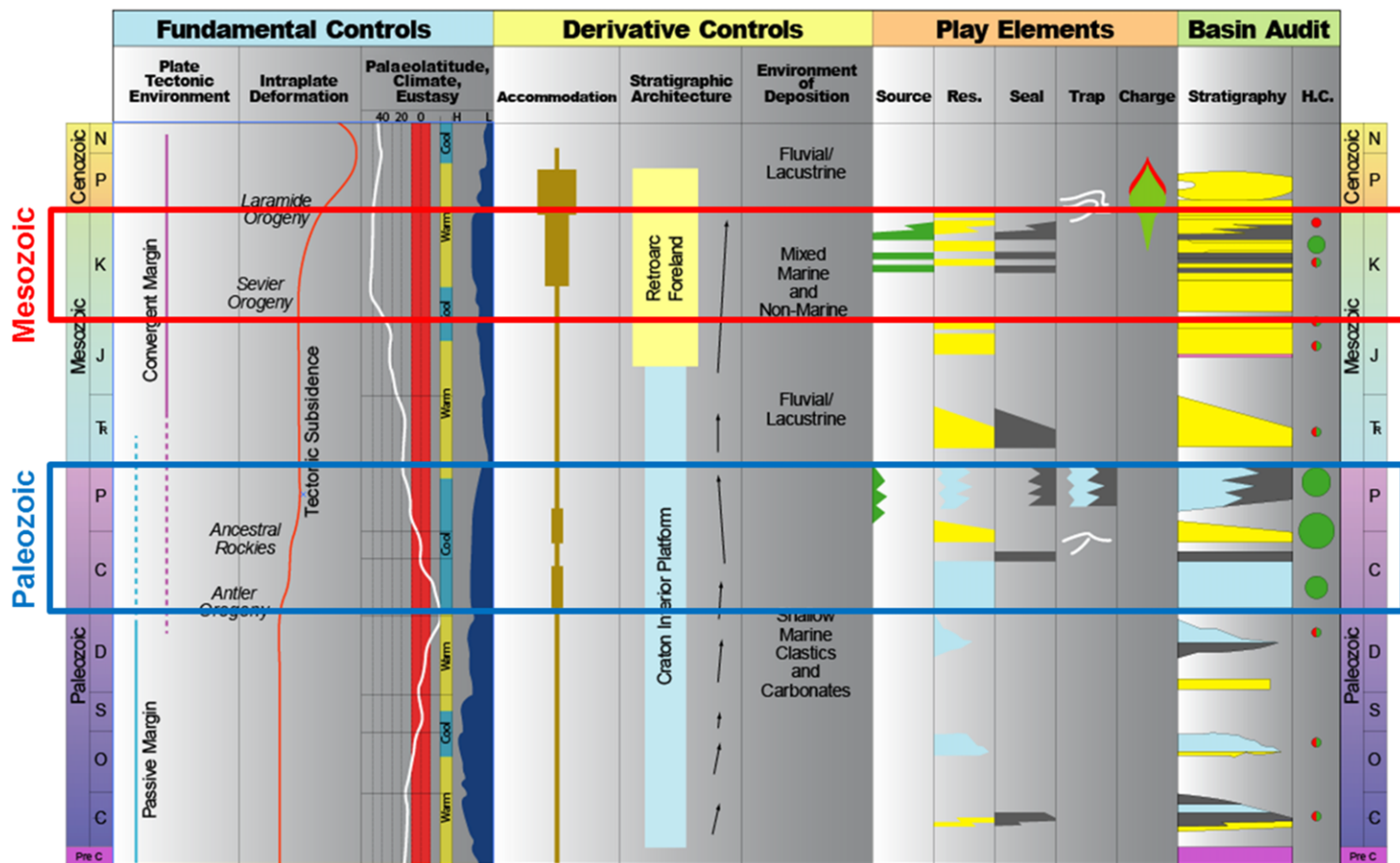


Fig. 2. Play summary chart for the Bighorn Basin. The play summary chart is used as a tool for genetic analysis of key petroleum systems elements and their relative timing. In the Bighorn Basin, there are two primary petroleum systems: (1) a Mesozoic system, outlined in red, in which local source rocks mature at the same time as local traps are forming; and (2) a Paleozoic system, outlined in blue, for which there is no apparent local source, and long-distance migration from source rocks to the west is likely to predate the formation of large structural traps, such as the one shown in Figure 1.

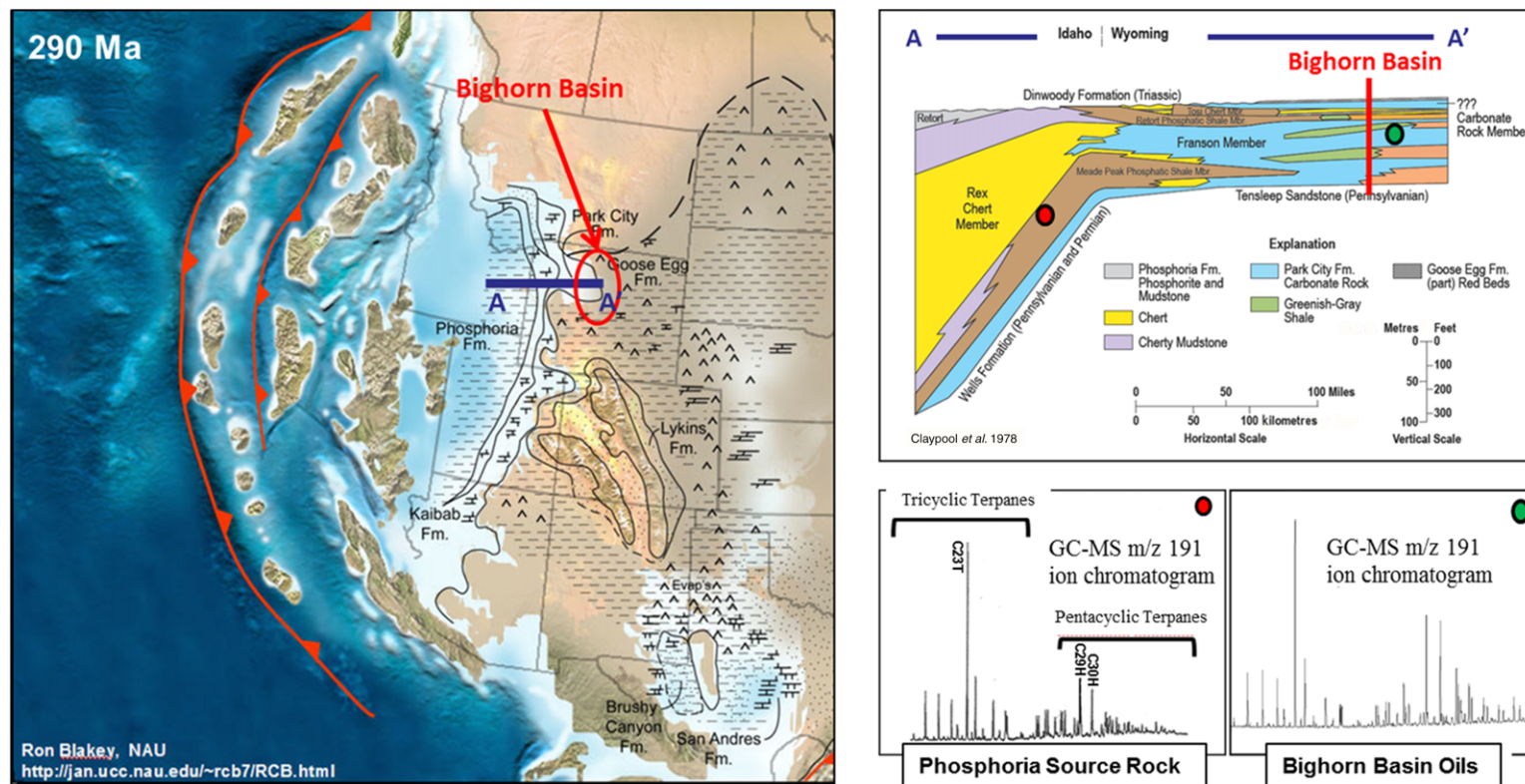


Fig. 3. Western North American palaeogeography at c. 290 Ma (Blakey 2011), at the time of deposition of key source rocks of the Phosphoria Formation. The geochemistry of oils reservoir in the Bighorn Basin correlates well with the geochemistry of Phosphoria source rocks, as illustrated by the m/z 191 chromatograms of Terpane biomarkers. The Phosphoria Formation is a largely a clastic-starved source rock that reaches TOC values of >20% along the western part of cross-section A–A'.

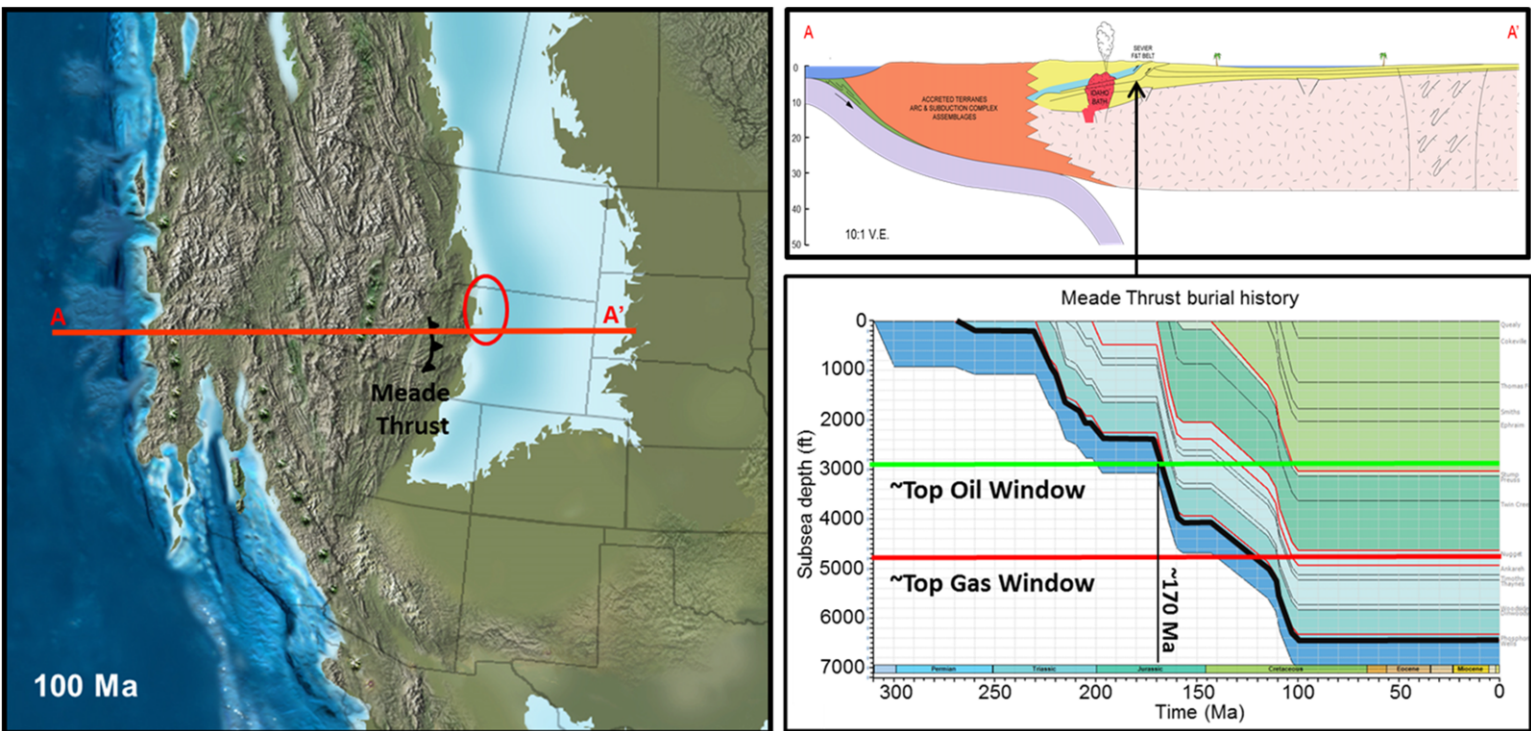


Fig. 4. Western North American palaeogeography at c. 100 Ma (Blakey 2011), which is a key time for the continuing maturation of Phosphoria source rocks and the long-distance migration of the resulting oils. A 1D burial history model from the footwall of the Meade Thrust shows that, at this locality, the Phosphoria (highlighted in black) is likely to have reached the oil window at c. 170 Ma. The model is supported by a K–Ar age of 178.6 ± 8 Ma from diagenetic illite in the Meade Thrust. V.E., vertical exaggeration.

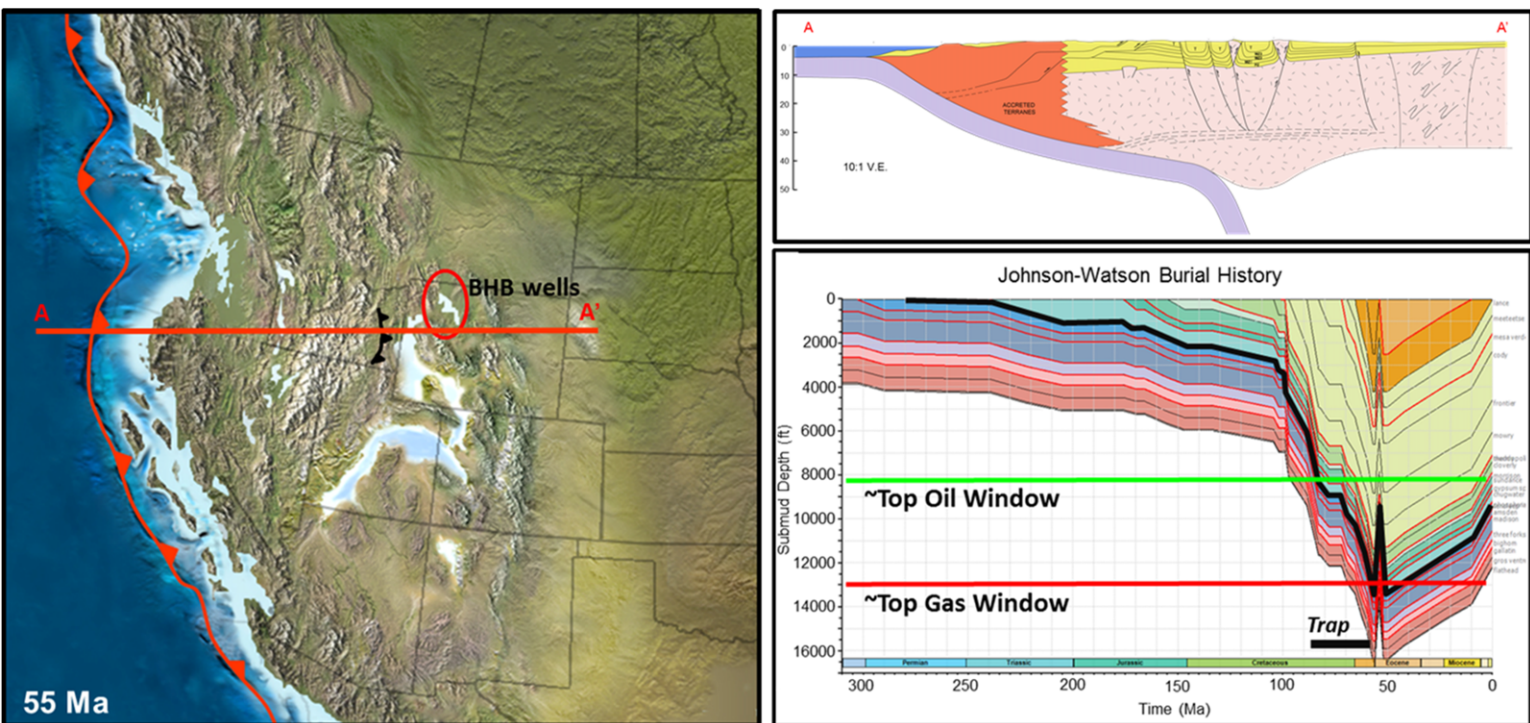


Fig. 5. Western North American palaeogeography at c. 55 Ma (Blakey 2011), during the development of the present-day Bighorn Basin (BHB) and its structural traps. The Sevier Foreland system was 'broken' by the basement involved uplifts, as shown in the crustal-scale cross-section. Large, basement-involved anticlinal traps developed in response to this deformation, and local Mesozoic-aged source rocks were buried and began to generate hydrocarbons, as shown by the burial history from a well in the Elk Basin Field (see Fig. 1).

well. What do geochemical tools have to offer to help us understand this complex petroleum system?

As noted in the previous section, and in other papers in this Special Publication, one of the new challenges for the next decade is the requirement to work with increasingly small and limited datasets in frontier environments. As an example, new high-resolution analytical techniques for hydrocarbon-bearing fluid inclusions now yield direct forensic evidence to constrain the source facies and maturity of petroleum source rocks, as well as the timing of migration and trapping. Paleozoic reservoirs in the Elk Basin oil field from the northern Bighorn Basin (Fig. 1) contain abundant hydrocarbon and aqueous fluid inclusions that reflect a range of fluid properties and suggest a complex charge history (Fig. 6, S. Becker, pers. comm., 2015). The oil and water inclusions display a wide range of homogenization temperatures. Bluish-white fluorescing inclusions in diagenetic calcite from one of the reservoir intervals, the Tensleep Formation, have homogenization temperatures of 60–100°C, and co-exist with water inclusions that have homogenization temperatures of 100–120°C. Brown and dull-yellow fluorescing inclusions from diagenetic anhydrite in the Phosphoria Formation have homogenization temperatures of 55–90°C, and co-exist with water inclusions that have homogenization temperatures of 105–110°C. The brown inclusions are consistent with lower API gravities associated with a biodegraded oil (Fig. 6). These trapping temperatures suggest that hydrocarbons began to be trapped as early as 80 Ma based on the thermal history for the Tensleep Formation at this location presented in Figure 4. This corresponds with the very early stages of trap development. Time-of-flight secondary ion mass spectrometry (ToFSIMS) analysis of individual inclusions (e.g. Siljeström *et al.* 2010) within these assemblages indicates that the oils in the inclusions are molecularly similar to those in the reservoir, and correlate well with a clastic-starved carbonate source rock (Siljeström *et al.* 2016).

Re–Os geochronology is one of the more significant recent developments in the analysis of the isotopic signatures of heavy metals, with applications to hydrocarbon systems analysis. This technique provide new constraints on the origin and history of hydrocarbons (Ventura *et al.* 2015; Georgiev *et al.* 2016). In this volume, Gao *et al.* (2017) discuss the systematics of the vanadium system, and here we describe results from the analysis of Re–Os in whole oils and asphaltenes from three wells in the NE corner of the Bighorn Basin (Fig. 1). The analyses were performed at the University of Arizona Re–Os laboratory (Kirk, pers. comm., 2017), using techniques similar to those published by Lillis & Selby (2013). They produced a well-constrained apparent isochron age of 185 Ma (Fig. 7), similar to both the age of

earliest hydrocarbon generation from the Phosphoria Formation to the west (Late Triassic–Early Jurassic: e.g. Sheldon 1967; Maughan 1984) and the Re–Os age of 211 ± 21 Ma published by Lillis & Selby (2013) for oils from the western Bighorn Basin. Both of these ages are considerably younger than the depositional age of the Phosphoria Formation (c. 285–250 Ma). Nonetheless, we are puzzled as to how to interpret these results. Although the oils all appear to have been generated from the same clastic-starved Phosphoria source-rock facies, they also appear to have been generated at different source-rock maturation stages (Fig. 7). Assuming that hydrocarbon migration occurred over a long period of time, in an open system, several scenarios could explain the data. Taking our data together with that of Lillis & Selby (2013), one scenario is that the Phosphoria-sourced oils were trapped and then remigrated into Laramide structures, mixing oils of different ages and maturities. Alternatively, these oils and Re–Os ages could also reflect early migration followed by bypass of later oil into updip traps, or some other process. Detailed analysis of individual fractions of the oil might help to resolve the alternative scenarios.

A relatively recent discovery of what we believe to be palaeoseeps in Campanian sandstones on the eastern side of the basin (Fig. 1) allows us to track the petroleum system from source all the way to seeps, and place additional constraints on migration timing. The mounds have a carbonate-cemented siltstone matrix with diverse macrofauna, capped with laminated algal carbonate and filled with calcite-lined fractures (Fig. 8). Assuming the features are palaeoseeps, they provide direct evidence of hydrocarbon migration in the Campanian (i.e. c. 80 Ma), similar to the time at which fluid inclusions were likely trapped. To find evidence for thermogenic hydrocarbons and their time of trapping, we completed preliminary isotopic analysis of released gases from matrix and fracture carbonates upon crushing. Matrix cements have a convincing contribution from thermogenic hydrocarbons, with $\delta^{13}\text{C}$ values for methane that range from –57 to –38‰. In contrast, vein cements appear to contain a greater contribution of biogenic methane, with $\delta^{13}\text{C}$ values for methane that range from –67 to –56‰. The only possible origin for thermogenic gas at this time is a distal source to the west, as local Mesozoic source rocks were still immature (Roberts *et al.* 2008). While we cannot rule out the possibility that the Campanian mounds were formed by, and charged with, biogenic methane, we believe these data provide direct support for the assertion that hydrocarbons sourced from the Phosphoria Formation continued to migrate to seeps in the Bighorn Basin during the Campanian.

While each of these techniques provide insights in to specific parts of the Paleozoic petroleum system

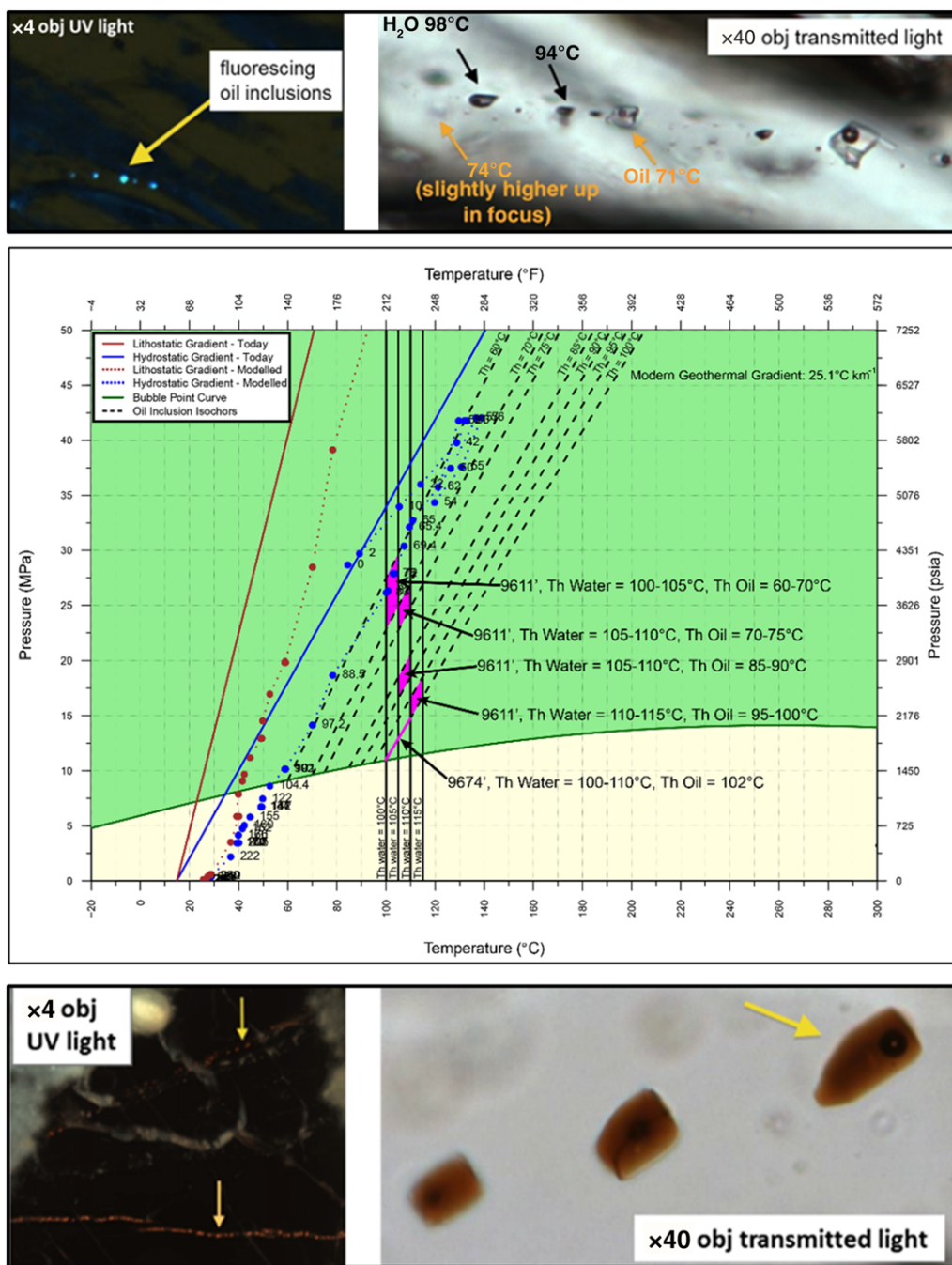


Fig. 6. Fluid-inclusion evidence for the timing of trap fill (S. Becker, pers. comm., 2015). Several populations of fluid inclusions from the Elk Basin Field are illustrated. Co-existing oil and water inclusions were used to estimate the pressure and temperature at the time of trapping, and were tied to time through a burial history model. Oil-inclusion isochores were calculated from pressure–volume–temperature (PVT) analysis of the present-day reservoir oils, and modelled hydrostatic and lithostatic pressure gradients based on the basin history in Figure 5. The results suggest that oil inclusions began to be trapped as early as 80 Ma. Trapping and post-emplacment alteration of fluid-inclusion oils is likely to have continued during the main stages of trap development, and possibly during mid-Tertiary exhumation.

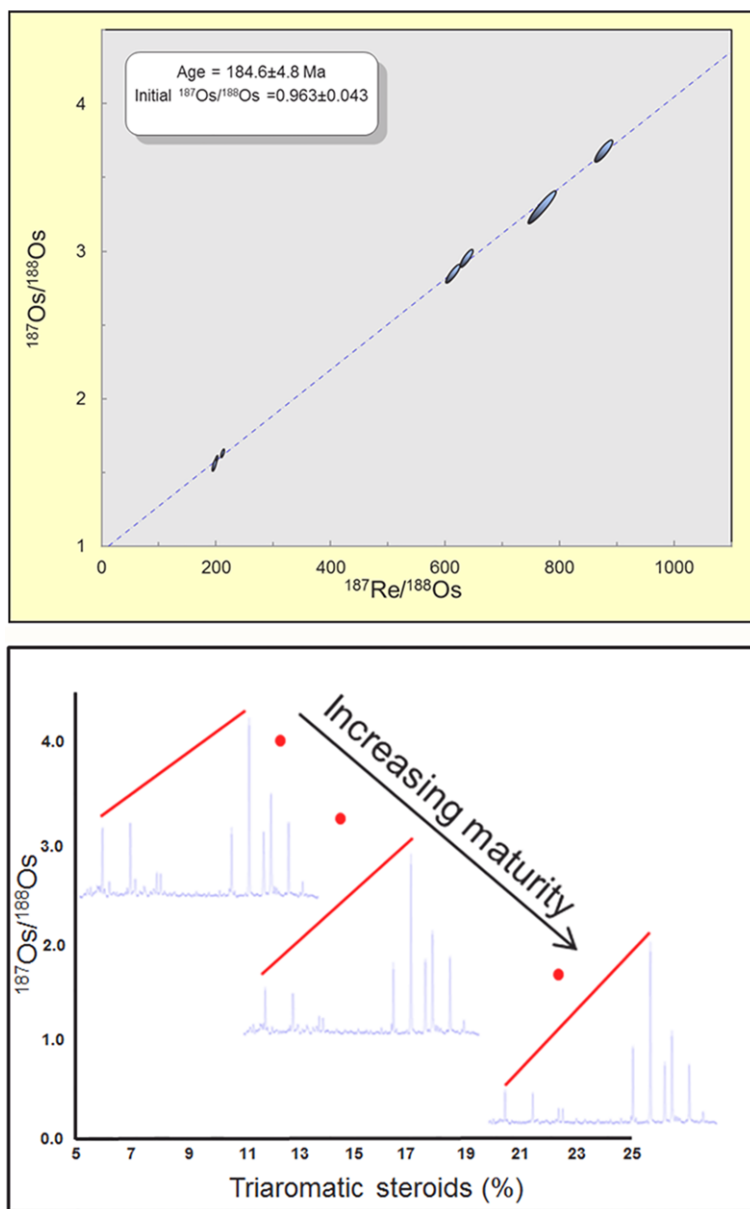


Fig. 7. Re–Os isotopic data from whole oils and asphaltenes sampled from the Byron, Garland and Little Polecat fields within the NE portion of the Bighorn Basin (Fig. 1). The data show a linear correlation on a Re–Os isochron diagram, and give a very well-constrained isochron age within error of the main array of 184.6 ± 4.8 Ma ($^{187}\text{Os}/^{188}\text{Os} = 0.963 \pm 0.043$), MSWD = 2.4. However, analysis of triaromatic steroids from the same oil samples suggests a trend of increasing maturity. Specifically, oils were generated from the same source facies, but at a different source-rock maturation stage, making it unlikely that all of the oils were trapped at the same time. The lowest maturity oils have the most radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratio, and the highest maturity oils have the least radiogenic $^{187}\text{Os}/^{188}\text{Os}$ ratio.

of the Bighorn Basin, it is only when they are all integrated that one gets a more complete understanding of the basin evolution and how it controls the

distribution of hydrocarbons in the basin. Hydrocarbons in the Paleozoic reservoirs have biomarker signatures that are consistent with being sourced from

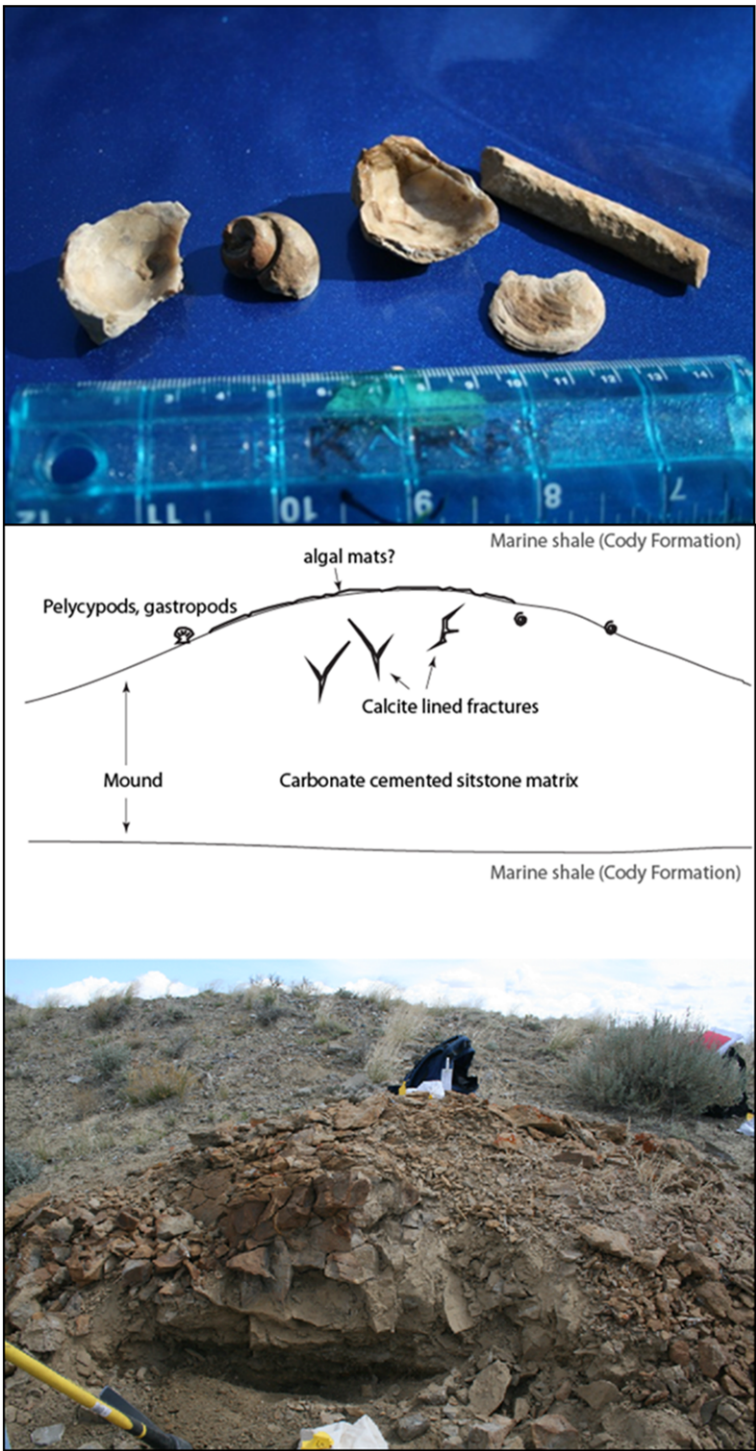


Fig. 8. Inferred palaeoseep mounds observed in Campanian mudstones (80 Ma) of the Cody Formation (Fig. 2) on the east side of the Bighorn Basin (Fig. 1). These macrofauna are consistent with, but not limited to, seep environments.

the Permian Phosphoria Formation, which requires oils to have migrated at least 100 km from the west and SW where the Phosphoria has high organic carbon contents. Basin modelling of this source kitchen to the west of the Bighorn Basin suggests that the Phosphoria Formation entered the oil window at c. 170 Ma. This is consistent with absolute age constraints from K–Ar dating of diagenetic illite

in this location. Furthermore, these Paleozoic oils have Re–Os ages that appear to be roughly consistent with the timing of hydrocarbon generation. However, the present-day traps that host these Phosphoria-sourced oils were not formed until after 85 Ma. One well-accepted migration model suggests that the oils were initially hosted in stratigraphic traps in the Phosphoria and Tensleep formations prior to

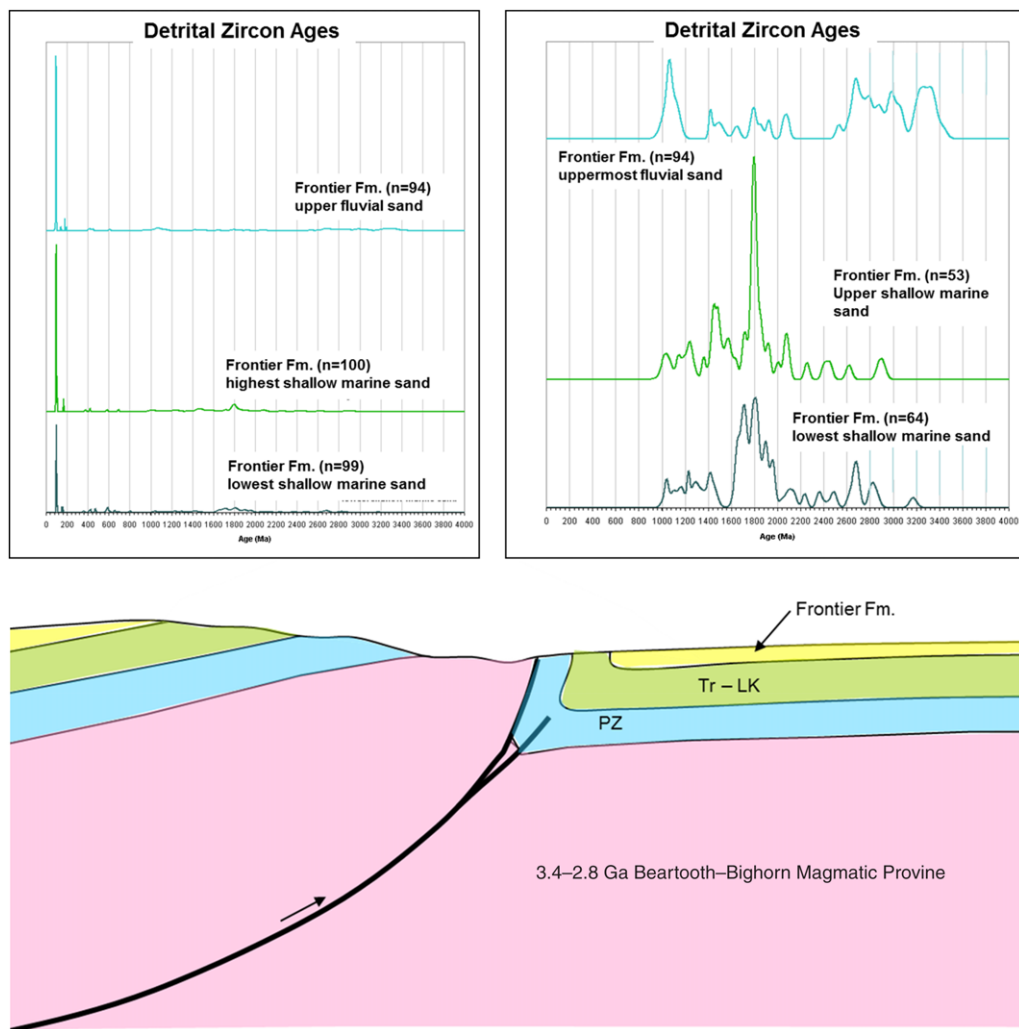


Fig. 9. Detrital zircon analysis of three shoreface/fluviol sands from the Cretaceous Frontier Formation (see Fig. 2) at the N Lazy S Ranch site (Fig. 1). Data were reproduced from May *et al.* (2013). The bottom two units are fine-grained quartzose sandstones, whereas the top unit is a coarse-grained arkosic sandstone. The zircon age probability distributions for all three samples are dominated by single clusters of young ages, consistent with the depositional age of the units. The age probability distribution for Precambrian grains in the three units is also plotted. The two lower samples display a broad spectrum of Proterozoic and Archean ages, with a prominent peak at 1800 Ma. The stratigraphically highest sample is unique in that it contains abundant Archean grains ranging from 3400 to 2600 Ma. The appearance of so many Archean grains, and the coarse-grained arkosic nature of the sandstone, suggests that these rocks were derived from Archean basement immediately to the west (Fig. 1). PZ, Paleozoic; Tr-LK, Triassic–Lower Cretaceous.

structuring and remigration (Stone 1967; Curry 2005), although potential top seals, and particularly the lateral seals for those traps, are lithologically heterogeneous (e.g. Campbell 1962; Paull & Paull 1986; Simmons & Scholle 1990). Alternatively, it is possible that incipient 'palaeostructures' enhanced the stratigraphic trapping mechanisms and improved the chances for 'catching' the early migrated hydrocarbons. Subtle Paleozoic structures have been recognized in the far NE portion of the basin (e.g. Simmons & Scholle 1990). We hypothesize that these types of subtle local features may have been more widespread than previously recognized.

To test the 'palaeostructure' hypothesis, we used yet another geochemical tool. The Frontier Formation (Fig. 2) is a major Mesozoic reservoir, deposited in the Sevier foreland at c. 100–90 Ma, when the volcanic arc to the west was active and first-cycle zircons were deposited with the sands. Zircons were analysed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Arizona LaserCron Center, using methods described by Gehrels *et al.* (2006). Detrital zircon age distributions for a site in the NW Bighorn Basin (Fig. 1), adjacent to the present-day Beartooth uplift, show a predominance of first-cycle zircons (Fig. 9) indicative of a young age, and consistent with the timing of Frontier deposition. However, these samples also contain a 3.4–2.7 Ga peak that can only be coming from the immediately adjacent basement (May *et al.* 2013), implying at least minor, local structural relief during Frontier deposition. The same sands are also poorly sorted and arkosic, indicating a local provenance. Our hypothesis is that subtle topographical highs began to form in the Middle Mesozoic on the western side of the basin, and helped to focus the pathways for hydrocarbons migrating from the west, within the underlying Phosphoria and Tensleep formations. These subtle highs would have enhanced the stratigraphic trapping potential within the Phosphoria and Tensleep formations, essentially creating combined structural–stratigraphic traps that either evolved to form the present-day structural traps and/or spilled hydrocarbons that remigrated into those traps.

In the preceding illustrative example, the combination of conventional and novel geochemical tools allowed us to better constrain the timing and pathways of hydrocarbon migration, but there are still unresolved issues. Geochemical approaches that could help address these issues include tools that constrain with high resolution: (1) the specific age of source rocks within a basin from the analysis of migrated fluids; (2) the distances that hydrocarbons have migrated from source to trap; and (3) the accumulation history of hydrocarbons, such as the timing of first charge to a trap, the identification of contributions of higher maturity fluids in mixed

oils and evidence of remigration from downdip structures.

Concluding remarks

We hope that the papers presented in this Special Publication provide those interested in petroleum systems analysis with a new perspective on how complex geological processes and signals can be understood and quantified. As hydrocarbon exploration continues to evolve and transition into increasingly complex and harsh environments, the need to glean the maximum information out of each sample continues to motivate analytical and technological developments in geochemistry and petroleum systems analysis. The current crop of technologies that are being developed and refined promise to provide a new generation of constraints that have the potential to be as important as those developed in the 1980s and 1990s. However, it is only when old and new techniques are integrated that can one hope to develop a more holistic understanding of the key elements and processes that contribute to the development of a robust petroleum system.

The integrated example of the Bighorn Basin presented here has been developed over many years at Exxon Mobil Corporation, and many people have contributed to this. We would like to thank Geoffrey Ellis for a thorough review and his suggestions to improve this manuscript. We thank Steve May, Robert Pottorf, Stephen Becker (ExxonMobil Upstream Research Company), Sebastian Dreyfus and Thomas Becker (ExxonMobil Exploration Company (a division of Exxon Mobil Corporation)) for significant contributions to this interpretation. We also thank James Kirk and Joaquin Ruiz for Re–Os analysis that was performed at the University of Arizona.

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